LA-UR -81-1646

TITLE: RAPID, DIRECT DETERMINATION OF ORGANIC SULFUR IN COAL USING
ELECTRON-PROBE MICROANALYSIS

AUTHOR(S): Robert Raymond, Jr.

MASTER

SUBMITTED TO: International Conference on Coal Science
September 7-9, 1981
WEST GERMANY

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663   Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

RAPID, DIRECT DETERMINATION OF ORGANIC SULFUR IN COAL USING ELECTRON-PROBE MICROANALYSIS

Robert Raymond, Jr.
Geosciences Division
Los Alamos National Laboratory
Los Alamos, NM, 87545, USA

Introduction

The electron probe microanalyzer (EPM) uses a finely focused electron beam that impinges on a polished sample, generally at 15-20 keV, producing x rays characteristic of the elements present in the sample. In general, EPM results should be accurate and reproducible to ±2% of the amount present for most major elements. Relative accuracy decreases with decreasing elemental concentrations. For elemental concentrations about 1 wt%, relative accuracy should be within ±5%. The following shows how the EPM may be used for quantitative analysis of organic sulfur in coal.

The EPM Approach

The American Society for Testing and Materials (ASTM) Standard Test Method D2492-68 for sulfur analysis in coal specifies the analytical determination of values for total, pyritic and sulfate sulfur. Organic sulfur is calculated by subtracting pyritic and sulfate sulfur from the total. The procedures are aimed at providing rapid, inexpensive, and reproducible data for coal utilization. The pyritic, sulfate, and organic sulfur contents reported by the processes adequately reflect the amount of sulfur that can be removed by sizing, specific gravity separation, and hindered settling techniques. But any error in total, pyritic or sulfate sulfur determination will show up as an error in organic sulfur determination. Reasons for error in pyritic sulfur determinations have been reported (Edwards et al., 1964; Greer, 1977).

EPM has important advantages over conventional methods of analysis for organic sulfur in coal: analysis by EPM is done directly, thus avoiding problems associated with calculating organic sulfur content by difference; organic sulfur contents of individual macerals can be measured in situ in a sample; and organic sulfur analysis with the EPM is both non-destructive and rapid.

Initially Raymond and Gooley (1978) calculated the organic sulfur content of a coal with the EPM using a mean modal analysis technique. In this process the mean organic sulfur content of each maceral type was determined and multiplied by the weight percent of that maceral in the dry coal sample. The sulfur contents contributed by individual maceral types were then summed to give the total organic sulfur content of the coal (Table I).

MACERAL	$\bar{x}$ wt% S_o	MACERAL wt%	wt% S_o/ MACERAL
Vitrinite	0.61	52.8	0.32
Pseudovitrinite	0.56	16.4	0.09
Fusinite	0.27	6.2	0.02
Semifusinite	0.44	6.2	0.03
Sporinite	0.64	6.0	0.04
Micrinite	0.59	2.8	0.02
Macrinite	0.51	0.7	(0.004)

Total S_o (dry) = 0.52 wt%

Table I: Comprehensive EPM method of organic sulfur analysis

To measure the validity of the EPM technique coals were chosen in which sulfate sulfur as determined by ASTM methods equaled zero and in which pyritic sulfur was minimal as determined by ASTM methods and as observed by optical microscopy. Since inorganic sulfur contents were small, any discrepancies between EPM and ASTM organic sulfur contents due to inaccurate pyrite or sulfate analysis should also be small. As can be seen in Table II the EPM analyses very closely approached those of the ASTM.

COAL	RANK	ASTM PYRITIC S	ASTM ORGANIC S	EPM ORGANIC S
U. Elkhorn #3	hvAb	0.01	0.61	0.63
Ohio #5	subC	0.01	0.92	0.94
L. Elkhorn	hvAb	0.03	0.52	0.50
Hazard #7	hvAb	0.03	0.51	0.58
U. Sunnyside	hvAb	0.06	0.59	0.66
Blind Canyon	hvAb	0.13	0.33	0.41
Dietz #3	subC	0.13	0.15	0.18

contents as dry wt%

Table II: ASTM/EPM comparative study

The comprehensive EPM method discussed above is extremely time consuming. The method requires point counting the sample to determine

the wt% of the various macerals. An oil immersion photomosaic has to be prepared for identification of analytical sites once the sample has been placed in the EPM. Finally, greater than 60 EPM analyses must be performed to determine the organic sulfur content of a single coal sample. Data derived from analysis of numerous coals using the comprehensive method, though, provided us with a better EPM approach.

The comprehensive method was performed on 29 coals that represented 27 seams from 13 states in the contiguous USA. Rank of the coals ranged from subbituminous C to low volatile; total sulfur contents ranged from 0.29 to 10.16 wt% (daf). The organic sulfur contents of the coals determined by the comprehensive EPM method are plotted vs the organic sulfur content of respective vitrinite components (Figure 1). The best linear fit of the data has a correlation coefficient of 0.99, a y-intercept of -0.03, and a slope of 0.98. Empirically, the organic sulfur content of a coal essentially equals the organic sulfur content of its vitrinite.
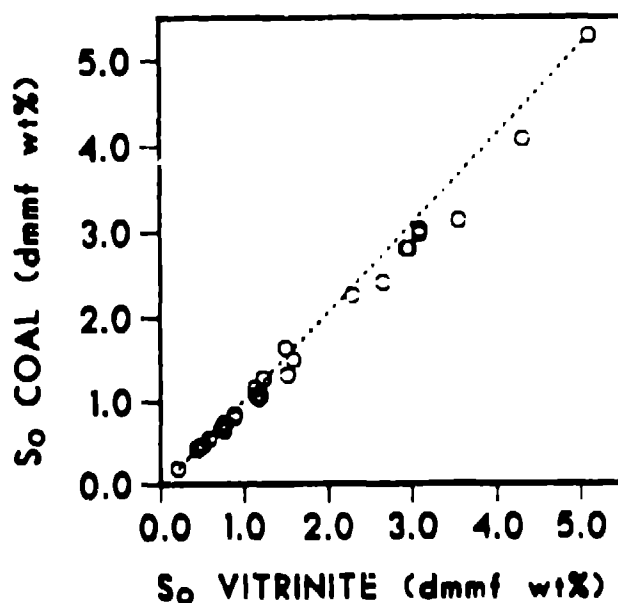

Figure 1:

Organic sulfur coal vs. organic sulfur vitrinite (all measurements by EPM)

Raymond (1979) showed that a general relationship exists in most coals with respect to organic sulfur contents of the macerals: sporinite, resinite $\geq$ micrinite, vitrinite > psuedovitrinite $\geq$ semi-fusinite $\geq$ macrinite > fusinite. How then can the vitrinite organic sulfur content be representative of all macerals present in a coal sample? In most of the 29 coals discussed above (as is the case in most coals) the vitrinite macerals dominate (Table III). Thus the vitrinite organic sulfur content has a major influence on the organic sulfur

	$\bar{x}$ wt%	RANGE
Vitrinite	78.5	38.9-92.2
Inertinite	17.3	9.1-38.9
Liptinite	3.7	0.0-19.2

Table III: Analysis of maceral constituents for 29 coals
(maceral wt% on a dmmf basis)

content of the coal. But what of the coals containing as little as 38.9 wt% vitrinite? Table IV contains the wt% of the various macerals found in two coals and the organic sulfur contents of those macerals. As can be seen in Table IV, the vitrinite organic sulfur contents approximate the organic sulfur contents determined from the weighted mean of the other macerals present. Therefore, as well as commonly being the most dominant maceral, the vitrinite contains an organic sulfur content equivalent to the mean of all the macerals.

U. Elkhorn hvAb Coal

	V	Pv	F	Sf	Ma	Mi	S	R
wt% of sample	38.9	2.2	7.1	5.3	13.2	13.3	17.6	2.4
wt% S_o	0.73	0.45	0.30	0.38	0.64	0.60	0.94	1.03

S_o Vit. = 0.73 S_o (wt'd $\bar{x}$) remaining macerals = 0.67 S_o coal = 0.69

Ohio #4 hvBb Coal

	V	Pv	F	Sf	Ma	Mi	S
wt% of sample	72.0	3.0	3.9	5.7	0.3	7.8	7.3
wt% S_o	2.93	2.56	0.73	1.51	0.92	2.90	3.89

S_o Vit. = 2.93 S_o (wt'd $\bar{x}$) remaining macerals = 2.50 S_o coal = 2.80

Table IV: Relationship between organic sulfur contents of vitrinite, remaining macerals, and whole coal (S_o wt% on dmmf basis) V = vitrinite, Pv = pseudovitrinite, F = fusinite, Sf = semi-fusinite, Ma = macrinite, Mi = micrinite, S = sporinite, R = resinite

There are two factors making it advantageous to measure the organic sulfur content of vitrinite to determine the organic sulfur content of a coal. The most obvious is that the number of EPM analyses will be fewer. For each of the coal samples listed in Table V, Raymond et al. (1980) analyzed up to 400 vitrinite grains for organic sulfur content both with and without the aid of photomosaics. Using a t-statistic

4

COAL	RANK	SULFUR wt% (daf)	n
Tebo	hvBb	9.37	13-14
Ohio #5	subC	1.02	10-12
U. Sunnyside	hvAb	0.69	5-6
L. Kittanning	low vol	2.81	7-9

Table V: Number of analyses (n) necessary to give a maximum desired variability when analyzing for organic sulfur with EPM

approach they calculated the number of analyses (n) for each run neces-sary to give a desired maximum variability of 10%, at the 95% confidence level, from the true mean as defined by 100 analyses. As can be seen in Table V, in no case was it necessary to analyze more than 14 vitrinite areas. The second advantage to analyzing only vitrinite is that Raymond et al. (1980) were able to achieve essentially identical results both with and without the use of photmosaics. Using texture and morphology to identify areas of vitrinite after the sample had been placed in the EPM was as successful as identifying the vitrinite using oil-immersion microscopy prior to analysis. Thus the need for photmosaics was eliminated.

The Rapid EPM Method

EPM analysis for organic sulfur content can be performed easily on -20 to -100 mesh coal samples. Samples need only be mounted in epoxy and polished as coal samples are commonly prepared for petrographic examination. 15 areas within non-contiguous vitrinite grains are ana-lyzed with the EPM. Without the need to produce a photomosaic, the organic sulfur content of vitrinite, and therefore of a coal, may be determined in less than 10 minutes.

To test the EPM method coals were analyzed for which the ASTM organic sulfur values were corrected for unextracted iron. As discussed by Suhr and Given (in press) such a correction would take into account the effect of any pyrite that remained unextracted following the ASTM Standard Method D2492-68. As can be seen from the data in Table VI, the EPM organic sulfur contents are very close to those of the corrected ASTM values.

Using the EPM method, the potential exists to achieve very rapid, multiple organic sulfur analyses, which in turn will allow for rapid, detailed measurements of variations in organic sulfur content occurring across coal seams.

L. KITTANNING hvAb/hvBb COAL

SAMPLE	S_o (diff.)	ASTM* S_o (corr.)	EPM S_o
1273	1.54	1.49	1.50
1276	2.12	2.07	2.09
1277	2.09	2.04	2.08
1279	0.55	0.44	0.60
1282	0.61	0.53	0.57
1299	1.28	1.19	1.09

Table VI: Coals containing pyrite - EPM S_o vs documented ASTM S_o
* ASTM data after Suhr and Given (in press) (all values as dry wt%)

References

Edwards, A.H., Jones, J.H., and Newcombe, W., "The extraction by nitric acid of pyrites from vitrains and coal samples," Fuel 43, 1964, pp.55-62.

Greer, R.T., "Coal microstructure and the significance of pyrite inclusions," in Scanning Electron Microscopy/1977/I, O. Johari (ed.), ITT Research Institute, Chicago, pp. 79-93.

Raymond, R.,Jr., "Relative abundances of common elements in coal macerals," in Microbeam Analysis, D.E. Newbury (ed.), San Francisco Press, San Francisco, pp. 105-110.

Raymond, R.,Jr, Davies, T.D., and Hagan, R.C., "Statistical validity for electron probe microanalysis of organic sulfur in coal," in Microbeam Analysis, D.B. Wittry (ed.), San Francisco Press, San Francisco, pp. 149-150.

Raymond, R.,Jr. and Gooley, R., "A review of organic sulfur analysis in coal and a new procedure", in Scanning Electron Microscopy/1978/I, O. Johari (ed.), SEM Inc., AMF O'Hare, IL, pp.93-107.

Suhr, N. and Given, P.H., "Reliability of determinations of pyritic iron in coals using standard procedures," Fuel (in press, 1981).